Domain Growth, Wetting and Scaling in Porous Media

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Abstract

The lattice Boltzmann (LB) method is used to study the kinetics of domain growth of a binary fluid in a number of geometries modeling porous media. Unlike the traditional methods which solve the Cahn-Hilliard equation, the LB method correctly simulates fluid properties, phase segregation, interface dynamics and wetting. Our results, based on lattice sizes of up to 4096×4096, do not show evidence to indicate the breakdown of late stage dynamical scaling, and suggest that confinement of the fluid is the key to the slow kinetics observed. Randomness of the pore structure appears unnecessary.

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It is well established that a binary fluid mixture undergoes phase separation if rapidly quenched from a high temperature phase to a point in the coexistence region. Moreover, when the size of the domains is much larger than the interfacial thickness, there is only one dominant length scale in the system [1]. This course of phase separation is completely changed when the binary fluid mixture is contained within a porous medium. Phase separation does not proceed to a macroscopic scale, and many small domains of the two phases are formed, even far below the critical point [2-4]. This lack of phase separation is poorly understood, and whether the observed small domain structure is due to the randomness of the pore structure or to the confinement of the mixture in small pores is controversial. One suggestion is that the randomness of the pore structure causes random-field Ising-like behavior, which gives rise to the small domains, leading to the metastability and the slow kinetics of domain growth that are observed in experiments [5]. An alternate suggestion is that confinement slows down domain growth [6]. A Monte Carlo study of the Ising model confined in a regular pore geometry allows for various long-lived metastable configurations ('plugs','capsules' and 'tubes') depending on temperature and strength of interaction, without any randomness included [7]. Recent work, using a Cahn-Hilliard description, investigated the kinetics of domain growth in an interconnected geometry resembling Vycor glass [8]. It concluded that the interconnected and tortuous geometry creates barriers to domain growth, and that there is breakdown of dynamical scaling at the late stage, implying the presence of many length scales. Moreover, since slow kinetics were obtained regardless of any surface interaction, the study inferred that it was unnecessary to invoke the random field model.

The above research has stimulated our interest in studying domain growth and wetting in porous media using a lattice Boltzmann method of simulation. We argue that this technique is a more appropriate tool to study the problem than the use of the

Cahn-Hilliard equation, or Ising type models. A number of geometries with imposed boundary conditions such as non-wetting, wetting, slip and no-slip conditions were investigated for lattice sizes of up to 4096×4096. We conclude that the evidence is not consistent with the breakdown of dynamical scaling, in the late time regime. In addition, we observe a slowdown of growth kinetics, regardless of the shape of the medium or conditions at the walls. This implies that, for times accessible to simulation, confinement of the fluid appears to be the key to the slowdown of kinetics, and that randomness of the pore geometry is not necessary.

Lattice gas and lattice Boltzmann methods provide computational environments with which to study hydrodynamic phase segregation using parallel computing techniques [9-14]. They simulate fluid properties, phase segregation and interface dynamics simultaneously, while complex geometries and their associated boundary conditions are implemented with simplicity. Other methods, such as molecular dynamics simulations, can accurately represent the dynamics of real fluids, but they are computationally intensive, limited to small systems, and are unable to access the late regime of spinodal decomposition. Methods that include hydrodynamic interactions, such as cell dynamical systems [15], and time dependent Ginzburg-Landau equations [16], approximate the dynamics with Langevin equations which are then solved numerically. In addition to being computationally intensive, these methods sacrifice the Navier-Stokes behavior of the fluid and the interface dynamics. On the other hand, LB methods simulate hydrodynamic phase segregation in a natural way, without the introduction of *ad hoc* relations between the order parameter fluctuations and the fluid dynamics.

The lattice Boltzmann method is a discrete in time and space, microscopic, kinetic description of the evolution of a *particle distribution function* of a fluid. Point particles move along the links of a lattice (hexagonal in two dimensions), obey certain collision

rules, and macroscopically mimic the Navier-Stokes equations in certain limits [12]. It has been used recently to study the effects of hydrodynamics on the late stage kinetics of a binary fluid mixture undergoing spinodal decomposition [17, 18]. The details of the steps involved in simulating the microscopic dynamics, such as streaming, collision, interface perturbation and recoloring, as well as comparison with experiment, are discussed in [19]. In contrast to the lattice Boltzmann method, the Cahn-Hilliard equation is more suitable for the study of binary alloys or glasses, rather than flow through porous media [1]. This is due to its inability to take into account hydrodynamic effects, which are important in the late stages of spinodal decomposition. Moreover, it assumes that the domain growth is the same, irrespective of which of the two fluids wets the surface. This assumption is valid only in the absence of wetting, the presence of which introduces an asymmetry such that the Ginzburg-Landau free energy is no longer symmetric in the order parameter. The Cahn-Hilliard equation, therefore, does not correctly model wetting, which may explain some of the differences between our results and those found in reference [8]. These difficulties are overcome in our use of the LB method which correctly simulates fluid-wall interfacial dynamics. Wetting is modeled by introducing a colored-particle interaction between walls and their nearest neighbor sites. This forces the wetting fluid in the porous medium to be attracted to the walls [19].

The two dimensional geometries that were studied included (a) a random distribution of disks with average radius 12 units, variance 4 units and porosity of 95%, (b) an interconnected and tortuous geometry with average domain size of 160 units and porosity 75% [8] and (c) periodic slits with pore radius of 16 and 64 lattice units. The geometry in (b) allowed a close comparison of results by different methods. In addition to studying various geometries, we also investigate the effects of both slip and no-slip conditions at the walls. The no-slip condition is accomplished by requir-

ing a "bounce back" of particles when they collide with a wall boundary, whereas the slip condition invokes a specular reflection of such particles. To study domain growth sizes, we define a local order parameter as the density difference between binary fluids, which we label red and blue:

$$\psi(\mathbf{x},t) = \rho_r - \rho_b = \sum_{i=0}^{6}(f_i^r(\mathbf{x},t) - f_i^b(\mathbf{x},t)).$$

Here, $f_i^r(\mathbf{x},t)$ and $f_i^b(\mathbf{x},t)$ are respectively the particle distribution functions for red (r) and blue (b) fluids at site $\mathbf{x}$ and time t moving along a link having direction i, and ρ_r and ρ_b are the red and blue fluid density. Also, $f_i(\mathbf{x},t) = f_i^r(\mathbf{x},t) + f_i^b(\mathbf{x},t)$ is the particle distribution function for the total fluid, where $i = 0,\ldots,6$ represents the velocity directions at each site of a hexagonal lattice. The state $i = 0$ corresponds to the portion of the fluid at rest. The LB equation for $f_i(\mathbf{x},t)$ can be written as

$$f_i^k(\mathbf{x}+\mathbf{e}_i, t+1) = f_i^k(\mathbf{x},t) + \Omega_i^k,$$

where k denotes a red or blue fluid species, and $(\Omega_i^k) = (\Omega_i^k)^c + (\Omega_i^k)^p$ is the collision operator consisting of a term representing the change in f_i^k due to collisions $(\Omega_i^k)^c$ and a term representing the color perturbation $(\Omega_i^k)^p$. The vectors $\mathbf{e}_i$ are the velocity vectors along the links of the lattice. The collision term $(\Omega_i^k)^c$ is chosen to have a single time relaxation form

$$(\Omega_i^k)^c = -\frac{1}{\tau}(f_i^{(k)} - f_i^{(eq)}),$$

where τ is the characteristic relaxation time and $f_i^{(eq)}$ is the local equilibrium distribution function [12, 13]. The surface tension inducing perturbation $(\Omega_i^k)^p$ and the recoloring procedure are chosen appropriately so that Laplaces's law holds for the model [19]. The mean free path in LB simulations is of the order of one lattice unit. The geometries we used have a pore radius of at least 16 units (greater than 50 for 4096×4096), therefore, finite size effects associated with the pore sizes should be

insignificant.

Simulations were carried out on lattices of sizes up to 4096×4096, for deep critical quenches with $\sum_{\mathbf{x}} \psi(\mathbf{x}, t) = 0$. The lattice was initialized with a random distribution of red and blue fluids in the pores, in order to introduce an initial fluctuation in the order parameter. Growth kinetics are characterized through the order parameter correlation function

$$G(r,t) =< \psi(r)\psi(0) > - < \psi >^2,$$

where $\langle\rangle$ denotes a spatial average. A characteristic domain size, $R(t)$, can be defined from $G(r,t)$ by its first zero crossing, and a structure factor can be defined from $G(r,t)$ by its Fourier transform. Note that the order parameter ψ is assigned a value of zero at the walls of the porous medium.

The domain morphology, with and without wetting, is shown in Fig. 1 for two geometries: the random distribution of disks of average radius 12 and variance 4 lattice units (geometry (a) defined above), and the tortuous geometry used in [8] (geometry (b) above). Elongated domains with a layer of wetting fluid are evident in Fig. 1a, whereas the characteristic plugs, cusps, and straight interfaces of the non-wet condition is seen in Fig. 1b. The variation of domain size as a function of time for the tortuous geometry of Fig. 1b is shown in Fig. 2a. During the early stages of growth ($t < 100$), where the two fluids are not completely separated, the system is unaware of the walls and therefore the growth for the bulk fluid case, non-wet walls, and wet walls show the same behavior. The domain size, $R(t)$, shows the expected $t^{1/2}$ law for early time [1]. As the dynamics evolves, however, the bulk fluid case assumes the expected $R(t) \sim t^{2/3}$ form ($\bigcirc$ signs) for the late stage period of time, while the presence of the walls begin to affect the domain growth for the other two cases ($\diamond$ and + signs). It is interesting to note that in all of the porous media that we studied, domains grew, for late time, as $t^{2/3}$ until their dynamics were strongly affected by the wall geometry. We

expect that this period of time may vary, depending upon the geometry, and may not exist at all for geometries with a large degree of confinement. Fig. 2a shows that late times for the bulk fluid case are in the range of $1000 < t < 2000$ where the domain size is $\sim$ 40-50 (much smaller than 4096). The slowdown is appreciable when the domain size is comparable to the characteristic size of the porous medium ($--$), defined by the first zero crossing of the pore-wall correlation function. When a fluid wets the walls, the domain growth (+ signs) is not as slow as the non-wetting case, and can exceed the characteristic pore size. The large system size considered here (4096×4096) did not allow us to access late enough times to observe this, however, it is clearly seen in Fig. 2b (1024×1024). Wetting effects allow the elongation of this phase, as well as making it possible to form a thin film surrounding the rock, increasing the period of time for domain growth. To investigate the effects of velocity boundary conditions on growth dynamics, we compare, in Figure 2b, the domain growth for a non-wet, slip boundary condition ($\bigcirc$ signs), a non-wet, non-slip boundary condition ($\diamond$ signs), and a wet, non-slip boundary condition (+ signs). We find that the domain growth of both the non-wet, slip and the wet, non-slip conditions exceeds the characteristic pore size ($--$) of the given geometry. It is of particular interest that the slip condition facilitates domain growth to a greater degree than in the wetting, no-slip case. This illustrates that confinement may be of more importance than wetting in the dynamics of domain growth slowdown.

The most interesting growth dynamics that we observed occur during the time interval between the $t^{2/3}$ growth region (t_i) and before phase segregation stops (t_f). Note that since we do not stir the fluids, the domain growth will ultimately cease. During $t_i < t < t_f$, there is a competing mechanism between the confinement of the geometry and the inertial motion of the separated domains with a curvature driven force [1]. The former will attempt to slow the fluid motion at the walls, whereas

the latter will try to keep the separated fluid domains in motion, allowing their aggregation to continue. Note that the non-slip condition confines fluid motion in both the normal and tangential directions, but the slip condition has confinement only in the normal direction. Clearly at this stage, the growth of the domain size will be slower than the bulk fluid case. An interesting phenomenon is seen in Fig. 2c where the domain growth is shown for both red and blue fluids in the presence of wetting. During this stage, the domain growth is not the same for the two fluids when the surface is preferentially wet for one fluid ($\Box$ signs) while not for the other ($\bigcirc$). On the other hand, when no wettability is present, domain growth for both the red and blue fluid is identical ($\triangle$). This emphasizes that the Cahn-Hilliard approach, which uses only the order parameter, does not model wetting correctly, and may not be an appropriate model for the phase separation process when wetting is important. Moreover, the behavior of domain growth in our simulations is different from those shown in [8], using the Cahn-Hilliard approach. In our results, the domain growth curves, in all cases, overlap for early times, and then deviate as the dynamics evolves. The results of [8], are, in fact, difficult to reconcile with the expected physical effects which are correctly modeled by the LB approximation in this paper.

The remaining question of importance, to be answered by our model, is whether or not domain growth in the late-time region ($t_i < t < t_f$) breaks the scaling laws as demonstrated by the previous study [8]. To answer this question, we examine the structure factor, $S(k,t)$, which is known to obey the dynamical scaling relation

$$S(k,t) = R(t)^d F(y)$$

for late times, in a wide variety of segregating systems [1]. Here $F(y)$ is the scaling function, with $y = kR(t)$, and d is the spatial dimension. The function $F(y)$ is plotted versus y in Fig. 3 for the bulk fluid and non-wet boundary condition (geometry (b)

above). The time interval is chosen to allow a difference in domain size for late times of approximately 30 for the bulk fluid case, and 50 in the tortuous porous medium. In both cases this represents an increase in growth by an approximate factor of two. Fig. 3 does not provide evidence to indicate the breakdown of dynamical scaling in the porous medium, contrary to the results reported in reference [8].

The other geometries that we have studied show similar growth and scaling behavior. We find that the degree of slowing down is a function of the pore size and porosity. Figure 4 shows the domain growth for two similar geometries: one having periodic slits of radius 16 units ($\diamond$ - non-wet, $\bigcirc$ - wet) and the other with 64 units ($\square$ - non-wet, $\triangle$ - wet). Note here that, even for the wetting cases, the domain size does not exceed the characteristic size of the porous medium, as seen in Figure 2b. This is because the confinement of the slit geometry only allows for growth in one dimension, after some initial time. In order to study slight deviations in the kinetics from the bulk case, we considered geometry (c) - a high-porosity medium (95%) consisting of a random distribution of disks. In results not shown here, we observed, for the non-wetting case, a slight slowdown in the kinetics, as expected, since the fluid experiences a certain degree of confinement. However, the domain growth in the wetting case is indistinguishable from growth of the bulk fluid. Our simulations indicate that confinement of the fluid within a pore geometry appears to be the key to the slowdown of kinetics. The form of the geometry, whether random, tortuous and interconnected or slit, does not appear to play a role in determining if slowdown occurs or not.

In conclusion, we have used a lattice Boltzmann model to study the kinetics of domain growth of a binary fluid in a number of two dimensional geometries resembling porous media. Our simulation results, carried out for large lattices, do not support the breakdown of late-time dynamical scaling, indicating the absence of many length

scales at late times. Our results suggest that confinement of the fluid in a region leads to the slow kinetics. Moreover, they indicate that the random field model, which requires some random component at a surface to obtain the slow kinetics, may not be relevant to the problem.

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Figure Captions

Figure 1. Domain morphology at $t = 4000$ for two geometries showing (a) wetting and (b) non-wetting cases. Figure (a) is a random distribution of disks of radius 12 units, variance 4 units and porosity 95%, and Figure (b) is an interconnected and tortuous geometry with porosity 75%, previously used in [8]. The rock is shown in white, and the two fluids in black and grey. The wetting fluid for (a) is black. Note the elongated domains with a layer of wetting fluid in (a), and the characteristic plugs, cusps, and straight interfaces of the non-wet condition in (b).

Figure 2. The variation of domain size as a function of time for the geometry of Fig. 1(b). (a) For a 4096×4096 lattice, the curves are for the bulk fluid ($\bigcirc$), wetting ($+$), and non-wet ($\diamond$) conditions. The dashed line at 160.8 represents the characteristic size of the porous medium, and the dotted line emphasizes the early ($t^{1/2}$) and late ($t^{2/3}$) growth of the bulk fluid. (b) The effects of the slip condition ($\bigcirc$) on domain growth versus two non-slip conditions: wet ($+$) and non-wet ($\diamond$) (1024×1024). The characteristic pore size is shown with the dashed line at 40.9. (c) A comparison of the growth for the red ($\square$) and blue ($\bigcirc$) fluids in the presence of wetting (1024×1024, red is wetting). The domain growth for the red and blue fluids overlap for the non-wetting case ($\triangle$) (1024×1024).

Figure 3. The scaled structure factor $F(y)$ as a function of y ($= kR(t)$) for (a) the bulk fluid and (b) the non-wet tortuous geometry [8] for 4096×4096. Scaling was investigated, for the bulk fluid, over time interval $[1000, 3000]$, and, for the porous medium, over time interval $[7000, 21000]$. Both of these time intervals represent respective domain growth of an approximate factor of two. A comparison of (a) and (b) makes it difficult to conclude that late-time dynamical scaling in the porous medium breaks down, as reported in reference [8].

Figure 4. The effects of pore size and wetting on the domain growth for a slit geometry with pore radii 16 units ($\diamond$ non-wet, $\bigcirc$ wet, characteristic pore size 25.6) and 64 units ($\square$ non-wet, $\triangle$ wet, characteristic pore size 101.3), using a lattice size of 1024×1024. Even for the wetting case, the domain size does not exceed the characteristic size of the porous medium. This is because the confinement of the slit geometry only allows for growth in one dimension, after some initial time.